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PII: S0040-4039(13)01958-8
DOI: http://dx.doi.org/10.1016/j.tetlet.2013.11.022
Reference: TETL 43817

To appear in: *Tetrahedron Letters*

Received Date: 25 April 2013
Revised Date: 16 October 2013
Accepted Date: 7 November 2013

Please cite this article as: Prodanov, M.F., Vashchenko, O.V., Vashchenko, V.V., A synthetic strategy toward branched oligomesogenic phosphonic acids: comparison of alternative pathways, *Tetrahedron Letters* (2013), doi: http://dx.doi.org/10.1016/j.tetlet.2013.11.022

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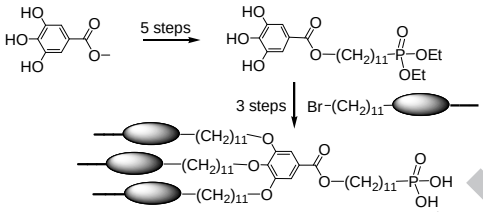

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A synthetic strategy toward branched oligomesogenic phosphonic acids: comparison of alternative pathways

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
Dendritic phosphonic acids
Promesogenic substituents
Hydrolysis
Esterification
Mesophase

ABSTRACT

This work is devoted to the elaboration of a practical scheme for the synthesis of dendritic derivatives of gallic acid containing a carboxylate-ω-alkylphosphonic acid group and three terminal promesogenic substituents. Two synthetic strategies toward the target compounds were examined that differ in the sequence of the introduction of the promesogenic units and ω-alkylphosphonic group.

Developing processes to combine the unique properties of inorganic nanoparticles (NPs) with anisotropic organic media such as liquid crystals (LCs) is currently of significant interest.[1-13] In spite of the long-term interest in such materials, highly-stable over time colloids have been only recently described.[7-15] Dendritic gallic acid derivatives of type **1** (**1a**, Figure1) were shown to be efficient stabilizers (surfactants) for such colloids.[13-15] Their structures comprise fragments typical for LC compounds (promesogenic units) and the spacer-separated phosphonic acid function as an anchoring group. The phosphonic acid linkage provides reliable binding for a wide variety of inorganic materials typically composing different types of NPs: glass and SiO_2,[16-19] magnetic Fe_2O_3, Fe_3O_4, CoO, Co, $Co(FeO_2)_2$,[20-22] semiconductors GaN, CdS, ZnS, ZnO,[23-27] ferroelectric $BaTiO_3$[28,29] and others.[30-33]

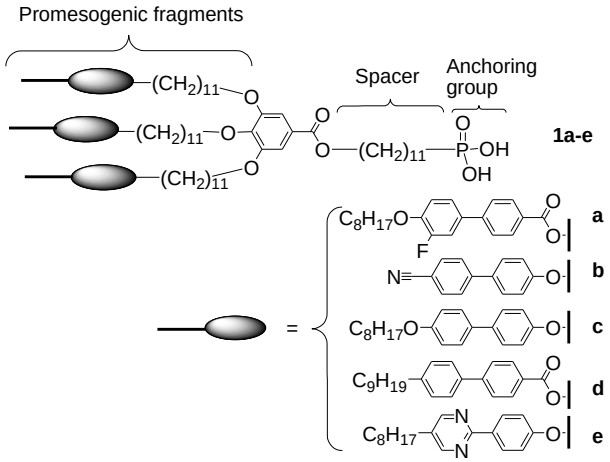

Figure 1. Structural formulae of efficient dendritic surfactants **1**

Despite the successful application of the surfactants of type **1**, their synthesis and isolation were not considered in detail. The closest described structural analogues of **1** either do not contain a phosphonic acid group or even possess a free carboxylic function of gallic acid.[34-46] The synthesis of a sole example of a dendritic gallic acid derivative with a spacer-separated phosphonic acid function has been described,[47] but this compound contained simple O-alkyl terminal substituents instead of the promesogenic units required here. Similar dendritic phosphonic acids were also

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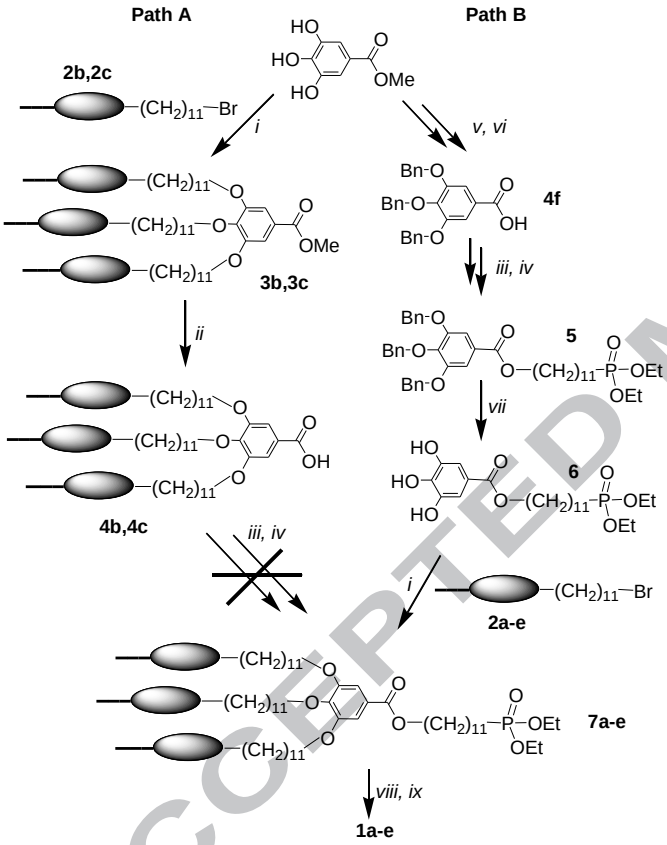
recently obtained starting from 5-(azidomethyl)-1,2,3-tris(dodecyloxy)benzene using the copper (I)-catalyzed Huisgen "click" cycloaddition.[48]

In all cases, these analogues were synthesized using an approach where O-alkylation of gallic acid was performed in the earlier steps whereas the carboxylic group was left free[34-37] or functionalized in the later stages.[38-45,47]

Herein we describe a practical approach for the synthesis of dendritic derivatives **1a-e**, and compare alternative approaches (Path A and Path B, Scheme 1).

Planning of the synthesis

In general, two synthetic strategies toward target compounds **1** can be proposed (Scheme 1). Path A is based on methods described in the literature. An advantage of this pathway is that most of the steps are well-documented for structural analogues of **1**.



Scheme 1. Generalized approaches for the synthesis of dendritic phosphonic acids of type **1**. The promesogenic unit assignment is the same as given in Figure 1. Reagents and conditions: (i) K_2CO_3, KI, zeolites CaA, MEK, reflux; (ii) **3b**: KOH, THF/EtOH, reflux; **3c**: CsOH, DMSO, 80 °C; (iii) 11-bromo-1-undecanol, DCC, DMAP, THF, r.t.; (iv) $P(OEt)_3$, 130 °C; (v) benzyl chloride, K_2CO_3, KI, MEK, reflux; (vi) NaOH, EtOH, reflux; (vii) H_2, 10% Pd/C, EtOAc, r.t.; (viii) TMSBr, CH_2Cl_2, 0 °C, r.t.; (ix) H_2O/THF, r.t.

However, the latter steps including introduction of the phosphoryl group is not described for compounds containing terminal promesogenic substituents. It is worth also noting, that several groups (ester, cyano, etc.), which are often included in the promesogenic fragment, can be unstable under the hydrolysis conditions (e.g., transformation of **3** into **4**, Scheme 1).

The majority of the steps in strategy B are not described in the literature, even for the synthesis of remote analogues of compounds **1**. Nevertheless, Path B seems to have some advantages over A. In particular, the introduction of the expensive promesogenic fragments occurs at a later stage, after the hydrolysis step. Therefore these fragments can include sensitive to hydrolysis substituents. Additionally, the path B allows wider variation of the promesogenic fragment structure.

Synthesis

The required promesogenic alkylating substrates (**2a-e**) were obtained by a multi-step synthesis that is described in detail in the Supplementary Material.

Initially, the more documented Path A (Scheme 1) was examined. The alkylation of methyl gallate was not complete under typical reaction conditions (K_2CO_3, prolonged reflux in MEK). Instead, a complex mixture of presumably mono-, di- and tri-alkylated products was formed. It was found, that in order to complete the reaction, freshly calcinated zeolites were required to remove water traces (for details of the procedure see the Supplementary Material). As a result, products **3b** and **3c** were obtained in 92% and 73% yields. The next step, the liberation of the carboxylic function of alkylated methyl gallates **3** proceeded smoothly only for cyano-derivative **3b,** following a previously described procedure[34] giving acid **4b** in 65% isolated yield. However, in the case of alkoxy-analogue **3c,** under the same conditions only the starting ester was recovered. The ester **3c** was also found to have unanticipated high resistance toward base-promoted hydrolysis under other conditions (Table 1).

Table 1. Hydrolysis of compounds **3b** and **3c** under different basic conditions

Entry	Starting material	Base	Conditions	Result
1	**3b**	KOH	THF / EtOH/ H_2O, reflux	65% [b]
2	**3c**	KOH	EtOH/H_2O, reflux	n/r[a]
3	**3c**	KOH	*i*-PrOH/ H_2O, reflux	n/r[a]
4	**3c**	LiOH	THF/ H_2O, reflux	n/r[a]
5	**3c**	KOH	THF / EtOH/ H_2O, reflux	n/r[a]
6	**3c**	Bu_4NOH	PhH/ H_2O, reflux	n/r[a]
7	**3c**	KOH	Bu_4NOH /*i*-PrOH/H_2O,reflux	n/r[a]
8	**3c**	KOH	Bu_4 NOH/PhH/H_2O, reflux	n/r[a]
9	**3c**	CsOH	DMSO/ H_2O, 80 °C	52%[b]
10	**3b**	CsOH	DMSO/ H_2O, r.t.	complex mixture

[a] No reaction according to TLC and HPLC.
[b] Isolated yield.

Assuming that the low reactivity of **3c** was caused by its limited solubility in alcoholic or water-alcoholic media (Table 1, entries 2 and 3), we tried to homogenize the reaction mixture by adding THF as a co-solvent. But even under prolonged refluxing the ester **3c** remained unchanged (Table 1, entries 4 and 5). Two-phase media were also inefficient (entries 6 and 8). Finally, we succeeded in obtaining acid **4c** using CsOH in DMSO/water as the solvent (entry 9, Table 1). It is worth noting, that even in such strong basic medium full conversion of the starting ester could only be achieved by heating at 80 °C for 4 hours; at 70 °C the reaction rate drops significantly, and below 60 °C it almost stops completely. However, these vigorous conditions are not generally applicable. In particular, in the case of compound **3b,** the cyano groups underwent substantial hydrolysis resulting in the formation of mono- and di-carbamoyl byproducts (see the Supplementary Material).

Further progress along Path A proved to be even more

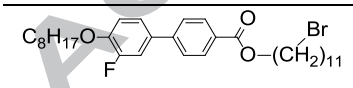
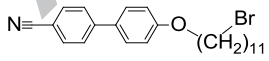
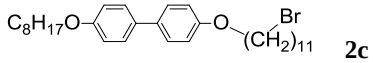
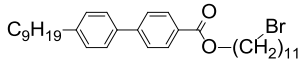
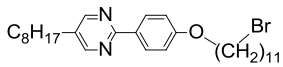
unsuccessful. Thus, all our attempts to involve acids **4b** or **4c** in the esterification with 11-bromo-1-undecanol using DCC/DMAP (Steglich-Hassner protocol[49]) failed. At ambient temperature the reactions did not occur (see the Supplementary Material, Table SM-1), presumably due to the very low solubility of the corresponding acids. Compound **4b** also did not react at elevated temperatures, while in the case of **4c**, the formation of only *N*-cyclohexyl gallic acid amide was detected. Varying the reaction conditions (solvent, temperature, reagents ratio) resulted in either recovery of the starting materials or formation of by-products (Table SM-1, Supplementary Material). Similar reaction patterns have been reported previously:[50-54] when the DCC-acid adduct reacts too slowly with an alcohol, the rearrangement of the corresponding O-acyl-ureas into *N*-isomers occurs followed by transformation into the undesired *N*-cyclohexylamide by-products. Our attempts to carry out *trans*-esterification of **3b** and **3c** with 11-bromo-1-undecanol under acid catalysis also failed and led to complex reaction mixtures. The reactions of the corresponding acid chlorides also did not result in formation of the desired compounds.

The failure in the synthesis of the target compounds **1** following Path A prompted us to change the strategy. The alternative synthetic approach depicted in Scheme 1 (Path B) employs a key intermediate **6** that can be converted into the desired surfactants of type **1** in two simple steps: alkylation of the phenolic hydroxy groups of the gallic acid fragment with promesogenic intermediates **2a-e** followed by mild de-O-alkylation of **7a-e** with TMSBr.[55]

The key compound **6** was obtained in five steps (see Scheme 1). Alkylation of methyl gallate with benzyl chloride followed by hydrolysis resulted in the formation of acid **4f** in high yield.[56] Esterification of **4f** with 11-bromo-1-undecanol using the Steglich-Hassner procedure,[49] and subsequent treatment with triethyl phosphite,[57] furnished smoothly diethylphosphonate **5**. Catalytic debenzylation of **5** over Pd/C resulted in the formation of key compound **6** in an overall yield of 54% based on methyl gallate.

The alkylation procedure (**6** → **7a-e**, Scheme 1) is similar to that described above for compound **3** (Path A, Scheme 1) and the full conversion of tri-hydroxy phosphonate **6** into the corresponding product **7** also required the application of zeolites (see Table 2).

Table 2. Synthesis of target compounds **1** and **7** according to Path B

Promesogenic alkylators	Yield (%)	
	6 → 7	**7 → 1**
 **2a**	64	69
 **2b**	70	90
 **2c**	62	78
 **2d**	65	74
 **2e**	86	91

It should be noted that purification of phosphonates **7a-e** can be easily achieved by flash chromatography instead of repeated crystallizations, as was required for purification of esters **3.** Moreover, the excess of the expensive alkylators **2a-e** (up to 0.5 equiv) can be recovered in high purities. The de-O-alkylation of phosphonates **7a-e** occured smoothly and furnished the desired phosphonic acids **1** in good yields (Table 2).

The phase behaviour of the dendritic phosphonic acids **1a-e** was studied using differential scanning calorimetry (DSC) and polarized optical microscopy (POM), see Table 3 and the Supplementary Material.

Table 3. Phase types (according to POM) and their transition temperatures (according to DSC in the cooling mode) for new oligomesogenic phosphonic acids **1**

	Phase transitions temperatures and enthalpy, °C (J/g)				
	Iso	N	Smectic phases		Cr or Glass
1a	• 79.3 (7.3)	–	• 68.0 (30.1)		•
1b	• 101.3 (5.8)	–	• 46.7 (0.9)	• 29.7 (8.7)	•
1c	• 230.5[a)]	–	• 199.0		•
1d	• 101.8 (6.6)	–	• 67.0 (19.1)		•
1e	• 87.2 (0.5)	• 84.0 (2.3)	• 72.0 (3.2)	• 56.0 (36.7)	•

[a)] measured using POM in the heating mode, the melting is accompanied with decomposition

All of the synthesized dendritic phosphonic acids show sequences of phase transitions which are reproducible over several cycles "heat-cool" except high-melting compound **1c**, which starts to decompose above its melting point. Using the POM and DSC data, it is difficult to determine definitely the mesophase types since very fine and untypical textures were observed (see the Supplementary Material). The assignment is also hampered by the nature of the studied compounds which are surfactants thereby providing vertical alignment even on glass substrates treated with polyvinyl alcohol. Taking into account the high viscosities of the birefringent melt and rather high iso-mesophase enthalpy values, the appearance of smectic type phase(s) can be assumed for almost all compounds (see Table 3). For compound **1e** the highest-temperature phase in the mesophase sequence can be assigned to the nematic (N) due to both relatively low viscosity and enthalpy values (0.5 J/g). More definite assignment requires further investigation and will be described elsewhere.

In conclusion, we have proposed a convenient and practical route for the synthesis of novel dendritic derivatives of gallic acid containing carboxylate-ω-alkylphosphonic acid groups as focal point and three terminal promesogenic substituents. The route is tolerant to hydrolysis-sensitive groups such as cyano and ester functions. The advantages of the proposed synthetic strategy (Path B) are revealed when the synthesis of a large range of dendritic phosphonic acids is required due to the fewer synthetic steps in comparison with Path A.

Acknowledgments

Financial support from the National Academy of Science of Ukraine (projects # 0110U003977, # 0112U004502 and research fellowship #288-12.10.2011). We also thank to Dr. N. Gorobets for the valued and fruitful discussions.

Supplementary Material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/...

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Graphical Abstract

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